



Microstructural Analysis of Poly(ethylene-co-propylene-co-1-butene) terpolymers by Multidimensional NMR Spectroscopy

การวิเคราะห์โครงสร้างทางเคมีในระดับโมเลกุลของ โพลี(เอทิลีน-โค-โพรพิรีน-โค-บิวทีน) เทอร์พอลิเมอร์ ด้วยเทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์สเปคโตรสโคปี

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บทคัดย่อ

ลักษณะทางกายภาพ คุณสมบัติการไหลและคุณสมบัติทางแสงของพอลิเมอร์ ขึ้นกับโครงสร้างทางเคมีในระดับโมเลกุลโดยเฉพาะอย่างยิ่ง ปริมาณของโมโนเมอร์และลำดับการจัดเรียงตัวภายในสายพอลิเมอร์ซึ่งจะส่งผลต่อคุณสมบัติเชิงกลของผลิตภัณฑ์ในขั้นสุดท้าย การศึกษาครั้งนี้เพื่อพัฒนาวิธีการศึกษาโครงสร้างทางเคมีในระดับโมเลกุลของสาร poly(ethylene-co-propylene-co-butene) ด้วยเทคนิค multidimensional นิวเคลียร์แมกเนติกเรโซแนนซ์สเปคโตรสโคปี ได้แก่ การทดลอง ^{13}C NMR การทดลอง pulsed-field-gradient (PFG) ^1H - ^{13}C heteronuclear single quantum coherence (gHSQC) การทดลอง pulsed-field-gradient (PFG) heteronuclear multiple bond coherence (gHMBC) และการทดลอง pulsed-field-gradient (PFG) heteronuclear single quantum coherence-total correlation spectroscopy (gHSQC-TOCSY) จากผลของการทดลองเหล่านี้ทำให้สามารถบ่งชี้โครงสร้างทางเคมีของสาร poly(ethylene-co-propylene-co-butene) ได้อย่างสมบูรณ์และนำไปสู่การศึกษาเชิงปริมาณได้อย่างถูกต้องยิ่งขึ้น

Abstract

Physical, rheological and optical properties of polymer depend on its molecular microstructure. Specifically, the monomer content and sequence distribution of polymer significantly affect the mechanical performance of the final product. To this base, Nuclear Magnetic Resonance Spectroscopy (NMR) has been introduced as a very powerful technique to study the microstructure of polymer. The purpose of this study was to develop a methodology to investigate the microstructure of poly(ethylene-co-propylene-co-butene) terpolymer by using multidimensional NMR spectroscopy, including pulsed-field-gradient (PFG) ^1H - ^{13}C heteronuclear single quantum coherence (gHSQC), heteronuclear multiple bond coherence (gHMBC), and heteronuclear single quantum coherence-total correlation spectroscopy (gHSQC-TOCSY). The combination of 1D and 2D NMR experiments, permit the characterization of the complex structure of poly(ethylene-co-propylene-co-butene) terpolymer. The completed ^{13}C NMR assignments provided in this work allow more accurate quantitative determination of the microstructure in these polymers

คำสำคัญ : พอลิเมอร์, นิวเคลียร์แมกเนติกเรโซแนนซ์สเปคโตรสโคปี

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1. Introduction

Copolymers are composed of two or more types of monomer units, which can be arranged in random, alternating, block or graft fashions. The arrangement of monomer units in a copolymer is controlled by the copolymerization conditions (e.g. catalyst, temperature), the monomer reactivity ratio, and the feed ratio. The information on the monomer sequence distributions can lead to an understanding of the kinetics and mechanism of copolymerization and the physical properties of the copolymers.

NMR spectroscopy is one of the most effective methods for the determination of monomer sequences. If two or more monomers are copolymerized in a statistically random manner, many possible monomer sequences can be formed. The ^1H and ^{13}C NMR spectra can be extremely complex due to the overlap of the resonances. The spectra are sensitive to the variations of the comonomer sequences. The resonances in high field NMR spectra are sensitive to pentad or even heptad monomer sequences, if stereo sequence effects are ignored; there are $2^5=32$ pentads and over 120 permutations of heptads. Thus, to assign resonance of a random copolymer becomes a challenging task. With the development of spectrometers, probe design and multidimensional NMR experiments, it is possible to assign the monomer sequence of a polymer without ambiguity.

Although there are extensive reports on the ^{13}C NMR determination of copolymers such as poly(ethylene-co-propylene)^[1-4], poly(ethylene-co-butene)^[5-7], and poly(propylene-co-butene)^[8,9], only few ^{13}C NMR studies of poly(ethylene-co-propylene-co-butene) terpolymer were investigated^[10-13].

2. Experimental

2.1 Preparation of Polymer Samples for NMR Analysis

Four ethylene/propylene/butene polymers (Polymer A, B, C and D) with low amounts of ethylene and 1-butene contents were provided by Thai Polyethylene, Ltd. About 0.04 g of terpolymer and 0.4 ml of 10% (w/v) of 1,4-dichlorobenzene- d_4 /trichlorobenzene solvent mixture were placed in a 5 mm NMR tube. A trace amount of hexamethyldisiloxane (HMDS) was added to serve as an internal chemical shift reference ($\delta_{\text{H}} = 0.09$ ppm, $\delta_{\text{C}} = 2.03$ ppm). The sample was spanned at 30 rpm in a Kugelrohr oven at 130°C until a clear homogenous solution was obtained.

2.2 Acquisition of 1D ^{13}C NMR spectra

The ^{13}C NMR spectra were obtained with Bruker Advance DPX 400 NMR spectrometer at 120 °C using a 5 mm broadband QNP probe, with a 9.57 μs 90 ° pulse, 17 kHz spectral width, 10,240 transients, 1 s acquisition time. The spectra were obtained with WALTZ-16 proton decoupling. Data were zero-filled to 512 k and exponential weighted with 1 Hz line broadening prior to Fourier transformation. The ^{13}C chemical shifts were reported relative to the reference shifts of internal hexamethyldisiloxane at 2.03 ppm.

2.3 Acquisition of 1D Quantitative ^{13}C NMR spectra

The quantitative ^{13}C NMR spectra were obtained with a 9.57 μs 90 ° pulse, 17 kHz spectral width, 2048 transients, 35s acquisition times. To eliminate NOE, spectra were obtained with an inverted gated WALTZ-16 proton decoupling. Data were zero filled to 512 k and exponential weighted with 1 Hz line broadening prior to Fourier transformation. The ^{13}C chemical shifts were reported relative to the reference shifts of internal hexamethyldisiloxane at 2.03 ppm.



2.4 Acquisition of 2D gHSQC NMR spectra at 400 MHz

2D NMR data were obtained with a BBLz probe at 120 °C on Bruker Advance DPX 400 NMR spectrometer. The Echo/Antiecho gradient selected HSQC NMR spectra were obtained with 90 ° pulse widths for ^1H and ^{13}C of 6.05 μs and 14.24 μs , respectively, a relaxation delay of 1.5 s, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$, ($^1J_{\text{CH}} = 130$ Hz), and the acquisition time of 0.214 s with simultaneous ^{13}C GARP decoupling, a 8.0 kHz spectral width in the ^{13}C (f_1) dimension and a 2.4 kHz spectral width in the ^1H (f_2) dimension; 8 transitions were averaged of 512 increments during t_1 . The two gradient pulses in the ratio 80 : 20.1 were used. The data were acquired in phase sensitive mode where CH and CH_3 cross-peaks were inverted relative to CH_2 cross-peaks. Linear prediction was used to forward extend the data two times its original length. Data were zero filled to provide a 2048 x 4096 matrix and processed with sine bell and sine square weighting before Fourier transformation.

2.5 Acquisition of 2D gHMBC NMR spectra at 400 MHz

Data were acquired with 90 ° pulse widths for ^1H and ^{13}C were 6.05 μs and 14.2 μs , respectively, a relaxation delay of 1.5 s, a 0.214 s acquisition time, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$ ($^1J_{\text{CH}} = 130$ Hz) with evolution delays of 80 ms (set to $1/(2 \times ^nJ_{\text{CH}})$), 32 transients were averaged for each of 512 t_1 increments. The evolution time was incremented to provide the equivalent of an 8 kHz spectral width in the f_1 dimension. A 2.4 kHz spectral width was used in the f_2 dimension. The three gradient pulses in the ratio 50 : 30 : 40.1 were applied. Linear prediction was carried out in the f_1 dimension to improve the digital resolution. Data were zero filled to provide a 2048 x 4096 matrix and processed with sine bell and shifted sine square weighting before Fourier transformation.

2.6 Acquisition of 2D gHSQC-TOCSY NMR spectra at 400 MHz

The States-TPPI gradient selected HSQC-TOCSY NMR spectra were obtained with 90 ° pulse width for ^1H and ^{13}C of 6.05 μs and 14.2 μs , respectively, a relaxation delay of 1.5 s, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$, ($^1J_{\text{CH}} = 130$ Hz), and an acquisition time of 0.21 s with simultaneous ^{13}C GARP decoupling ; 32 transients were averaged for each of 2'512 increments during t_1 with the evolution time incremented to provide the equivalent of 8 kHz spectral width in the ^{13}C (f_1) dimension and a 2.4 kHz spectral width in the ^1H (f_2) dimension. A spin-lock pulse was applied for a period of 60ms with MLEV-17 modulation. The three gradient pulses in the ratio 80: 30 : 20.1 were used. Linear prediction was used to forward extend the data. Data were zero filled to provide a 2048 x 4096 matrix and processed with sinebell and shifted sine square weighting before Fourier transformation.

2D NMR data including; gHSQC, gHMBC, gHSQC-TOCSY of terpolymerA were also obtained on the 500 MHz NMR instrument. The parameters of these experiments were as following.

2.7 Acquisition of 2D gHSQC NMR spectra at 500 MHz.

2D NMR data were obtained with indirect detection probes at 120 °C on Varian INOVA 500 MHz NMR spectrometer. The gradient selected HSQC NMR spectra were obtained with 90 ° pulse widths for ^1H and ^{13}C of 6.13 μs and 13.20 μs , respectively, a relaxation delay of 1.5 s, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$, ($^1J_{\text{CH}} = 125$ Hz), and an acquisition time of 0.205 s with simultaneous ^{13}C GARP decoupling, 8.1 kHz spectral width in the ^{13}C (f_1) dimension and a 2.5 kHz spectral width in the ^1H (f_2) dimension; 8 transitions were averaged for each of 2'512 increments during t_1 . The data were acquired in phase sensitive mode where CH and CH_3 cross-peaks are inverted relative to CH_2 cross-peaks. Linear prediction was used to forward extend the data two times its original length. Data were zero filled to provide a 2048 x 4096 matrix and processed with sine bell and sine square weighting before Fourier transformation.

2.8 Acquisition of 2D gHMBC NMR spectra at 500 MHz.

Data were acquired with 90° pulse widths for ^1H and ^{13}C were 6.13 μs and 13.2 μs , respectively, a relaxation delay of 1.0 s, a 0.205 s acquisition time, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$ ($^1J_{\text{CH}} = 140$ Hz), 16 transients were averaged for each of 512 t_1 increments. The evolution time was incremented to provide the equivalent of an 8.1 kHz spectral width in the f_1 dimension. A 2.5 kHz spectral width was used in the f_2 dimension. Linear prediction was carried out in the f_1 dimension to improve the digital resolution. Data were zero filled to provide a 2048 x 4096 matrix and processed with sine bell and shifted sine square weighting before Fourier transformation.

2.9 Acquisition of 2D HSQC-TOCSY NMR spectra at 500 MHz.

The States-TPPI gradient selected HSQC-TOCSY NMR spectra were obtained with 90° pulse width for ^1H and ^{13}C of 6.13 μs and 13.2 μs , respectively, a relaxation delay of 1.0 s, a delay Δ set to $1/(2 \times ^1J_{\text{CH}})$ ($^1J_{\text{CH}} = 125$ Hz), and an acquisition time of 0.205 s with simultaneous ^{13}C GARP decoupling ; 8 transitions were averaged for each of 2'512 increments during t_1 with the evolution time incremented to provide the equivalent of 8.1 kHz spectral width in the ^{13}C (f_1) dimension and a 2.5 kHz spectral width in the ^1H (f_2) dimension. A spin-lock pulse was applied for a spin-lock field of 8.0 kHz with MLEV-17 modulation. Linear prediction was used to forward extend the data. Data were zero filled to provide a 2048 x 4096 matrix and processed with sine bell and shifted sine square weighting before Fourier transformation.

3. Results and Discussion

3.1 Structure and Nomenclature

The carbon chemical shift assignments in this work are labeled based on nomenclature first defined by Carman^[14] which was modified later by Dorman^[15] and Randall^[6]. Methylene carbons along the backbone of an ethylene/propylene/butene terpolymer chain are identified by a pair of Greek letters to indicate the distance to the nearest branch points in either direction. Carbons in the side-chain branches are identified by iB_n and iB_m where 'i' indicates the position in the branch, starting with the methyl carbon in position 1, and the subscript 'n' and 'm' indicate the length of the branch (e.g. B_1 for propylene units and B_2 for butene units). The methylene carbon between different branches are named by xyB_nB_m where x and y are two Greek letters indicated the distance to the B_n and B_m branches, respectively. The saturated carbons at the end of the main chain are identified as 1s(CH_3), 2s(CH_2), 3s(CH_2), etc. Figure 1 shows an example of carbon atom identification.

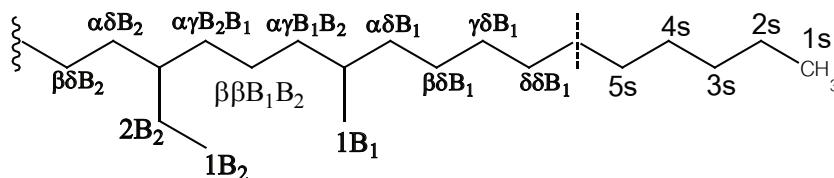


Figure 1 Nomenclature of ethylene/propylene/butene terpolymer

The capital letters "E", "P" and "B" are used to indicate ethylene, propylene and butene monomer units, respectively, to describe the monomer sequence distributions.



When two or more branches are in adjacent positions, the relative stereochemistry of the neighboring chiral centers also becomes important. The relationship between monomer units in a dyad is termed *meso* or *m* when two neighboring asymmetric carbons have the same stereochemical configuration. The relationship between monomer units in a dyad is termed *racemic* or *r* when two neighboring asymmetric carbons have opposite stereochemical configuration.

3.2 ^1H NMR of poly(ethylene-co-propylene-co-butene)

The 400 MHz ^1H NMR spectrum of ethylene/propylene/butene terpolymer is shown in Figure 2. The spectrum shows three broad resonances due to the overlaps arising from the strong coupling among the many main chain and the side chain protons with similar chemical shifts. The peaks appearing between 0.8-1.10 ppm correspond to methyl proton resonances from methyl and ethyl branches. The $\alpha\alpha$ methylene protons of **PP** and **PB** dyads also arise in this region. The peaks appearing around 1.3 ppm and 1.6 ppm correspond to methylene and methine protons, respectively.

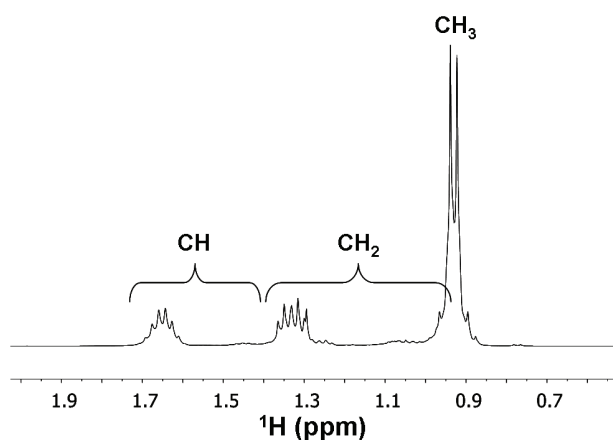


Figure 2 The 400 MHz ^1H NMR spectrum of poly(ethylene-co-propylene-co-butene) terpolymer.

3.3 The ^{13}C NMR of poly(ethylene-co-propylene-co-butene)terpolymers

The 100 MHz ^{13}C NMR spectra of terpolymers A, B, C and D are shown in Figure 3, (a) terpolymer A (ca. 90.80 % 1-propylene, 3.52% - ethylene, 5.72 % 1-butene), (b) terpolymer B (ca. 93.80 % 1-propylene, 4.27% - ethylene, 1.93 % 1-butene), (c) terpolymer C (ca. 89.70 % 1-propylene, 4.39% - ethylene, 5.90 % 1-butene) and (d) terpolymer D (ca. 92.90 % 1-propylene, 4.89% - ethylene, 2.25 % 1-butene). These polymers have predominantly *isotactic* sequences mainly from propylene units. The variations among these polymers are observed due to the differences in tacticity and monomer sequence distribution. The chemical shift assignments of terpolymer A, B, C and D are listed in Table 1. They were initially assigned based on the literature^[7-13], the use of 2D NMR experiments (gHSQC, gHMBC and gHSQC-TOCSY) assist in confirmation of most of the assignments. In addition, corrections and new assignments of the resonances from these terpolymers are also provided by these new data.

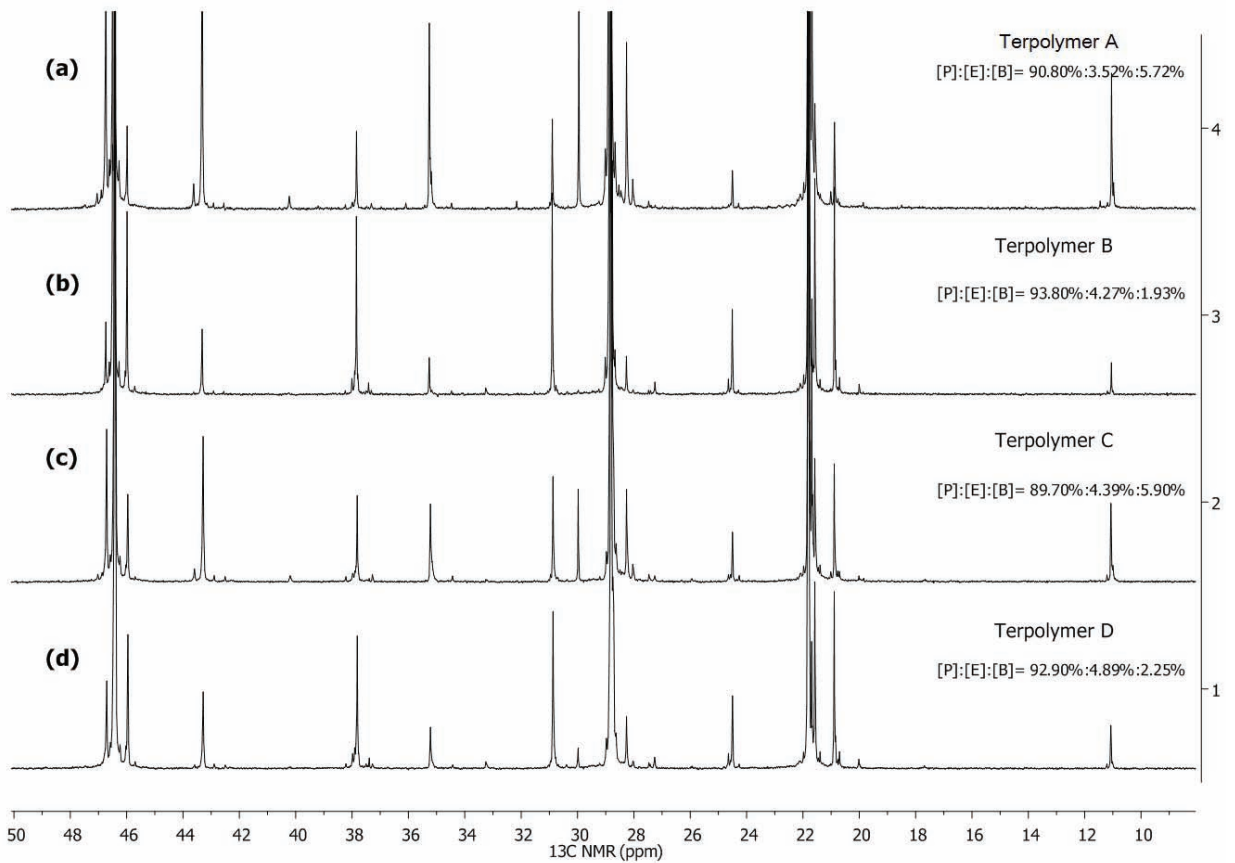


Figure 3 The 100 MHz ^{13}C NMR spectra of terpolymers A, B, C and D at 120 °C

- (a) terpolymer A (ca. 90.80 % 1-propylene, 3.52 % - ethylene, 5.72 % 1-butene);
- (b) terpolymer B (ca. 93.80 % 1-propylene, 4.27 % - ethylene, 1.93 % 1-butene);
- (c) terpolymer C (ca. 89.70 % 1-propylene, 4.39 % - ethylene, 5.90 % 1-butene)
- and (d) terpolymer D (ca. 92.90 % 1-propylene, 4.89 % - ethylene, 2.25 % 1-butene).

The expansion of the $\delta\delta$ methylene carbons (at $\delta_c = 29.96$ ppm) and methine carbons (at $\delta_c = 30.85$ ppm) from the ^{13}C NMR spectra of terpolymers A, B, C and D shows in Figure 4. The $\delta\delta$ methylene carbon appears in terpolymer A and C but slightly detected in terpolymer B and D. The evidences suggest that terpolymer A/C and terpolymer B/D could be produced with the similar processing condition.

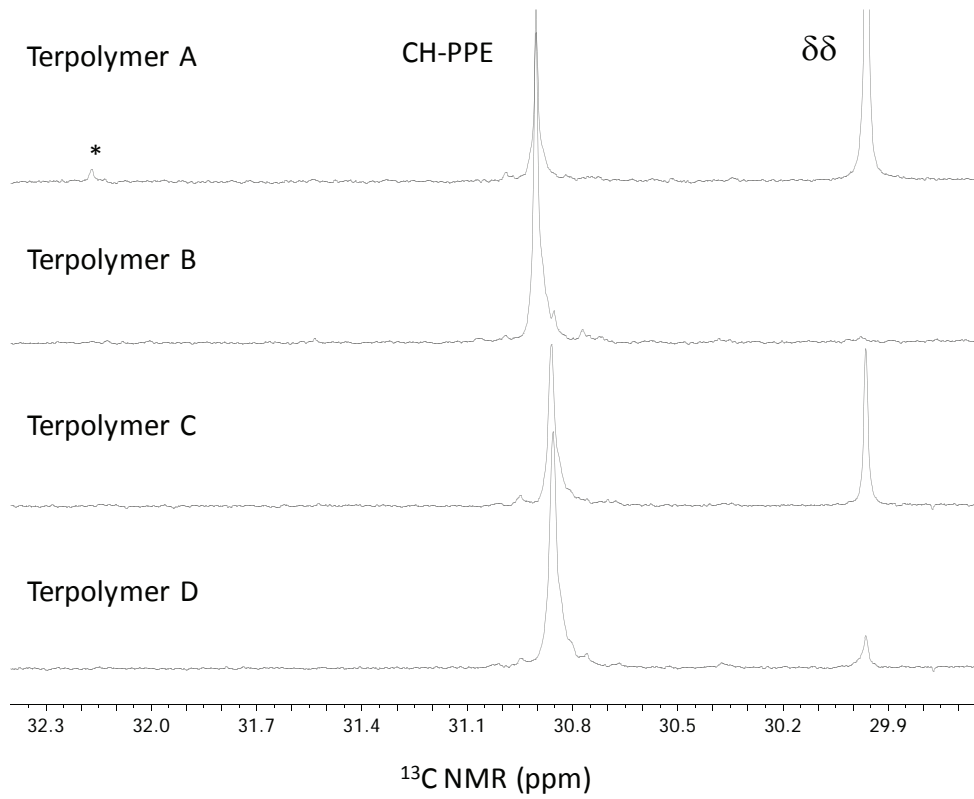


Figure 4 The expansions of the $\delta\delta$ and CH-PPE regions from the 100 MHz ^{13}C NMR spectra of terpolymer A, B, C and D.

Table 1 The chemical shift assignments of terpolymers A, B, C and D.

Region	Peaks No.	Carbon	Polymer sequence	¹³ C (ppm)			
				Terpolymer A	Terpolymer B	Terpolymer C	Terpolymer D
M	73	$\alpha\alpha B_1$	BPPB	47.06	-	47.01	-
	72	$\alpha\alpha B_1$	PPPPPPP (<i>xmmm</i> x)	46.91	-	46.86	-
	71	$\alpha\alpha B_1$	BPPP	46.75	46.75	46.70	46.70
	70	$\alpha\alpha B_1$	PPPPPPP (<i>xmmm</i> x)	46.62	46.62	46.57	46.57
	69	$\alpha\alpha B_1$	PPPPPPP (<i>xmmm</i> x)	46.51	46.51	46.46	46.46
		$\alpha\alpha B_1$	BPPPPB				
	68	$\alpha\alpha B_1$	PPPPPB	46.48			
	67	$\alpha\alpha B_1$	PPPPP (<i>mmmm</i>)	46.45	46.45	46.40	46.40
	66	$\alpha\alpha B_1$	PPPPP (<i>rr</i>)	46.28	46.28	46.22	46.22
	65	$\alpha\alpha B_1$	PPPE (<i>m</i>)	45.99	45.99	45.94	45.94
64	$\alpha\alpha B_1$	EPPE (<i>m</i>)	-	45.72	45.69	45.69	
L	63	$\alpha\alpha B_1B_2$	BPPB	43.63	-	43.58	-
		$\alpha\alpha B_1B_2$	PBPB				
	62	$\alpha\alpha B_1B_2$	BBPP	43.33	43.33	43.28	43.27
		$\alpha\alpha B_1B_2$	PPBP (<i>m</i>)				
		$\alpha\alpha B_1B_2$	BBPB				
		$\alpha\alpha B_1B_2$	BBPE				
	61	$\alpha\alpha B_1B_2$	PBPE	42.92	42.92	42.88	42.88
	$\alpha\alpha B_1B_2$	EBPP					
60	$\alpha\alpha B_1B_2$	EBPE	42.57	42.57	42.49	42.48	
K	59	$\alpha\alpha B_2$	PBBP (<i>r</i>)	40.24	-	40.19	-
J	58	$\alpha\gamma B_1$	XPEPX	38.24	38.24	38.21	38.21
	57	$\alpha\gamma B_1$	XPEPX	38.00	38.01	37.97	37.97
	56	$\alpha\gamma B_1$	XPEPX	37.91	37.91	37.89	37.89
	55	$\alpha\gamma B_1$	XPEPX	37.88	37.89	37.85	37.85
	54	$\alpha\gamma B_1$	PPEPP (<i>m</i>)	37.84	37.85	37.81	37.81
		$\alpha\gamma B_1$	PPEPP (<i>m</i>)	-	37.80	37.76	37.76
	53	$\alpha\delta B_1$	PEE	-	37.42	-	-
	52	$\alpha\delta B_1$	PEE	-	-	37.38	37.38
	51	$\alpha\delta B_1$	PEE	37.33	37.33	-	-
	50	$\alpha\delta B_1$	PEE	-	-	37.27	37.27
I		*	unusual structure	36.10	-	-	-
	49	CH	PPBP	35.26	35.26	35.21	35.21
	48	CH	XPBPX	35.23	35.23	-	-
	47	CH	PBB	35.19	-	overlap	overlap
H	46	$\alpha\gamma$	BEB	34.48	34.48	34.42	34.42
G	45	CH	EPE	-	33.24	33.24	33.24
		*	unusual structure	32.17	-	-	-
F	44	CH	XPPEX	30.90	30.90	-	-
		CH	XPPEX	-	30.85	30.86	30.86
		CH	XPPEX	-	30.77	-	30.77
E	43	$\delta\delta$	(EEE) _n	29.96	-	29.96	29.96
D	42	CH	PPP (<i>xx</i>)	29.02	29.02	28.96	28.96
	41	CH	PPB +BPB	28.90	28.90	28.85	28.85
	40	CH	PPPPP (<i>mmmm</i>)	28.86	28.86	28.80	28.80
	39	CH	PPPPP (<i>mmrr</i>)	28.80	28.80	28.73	28.73
	38	CH	PPPPP (<i>mmrr</i>)	28.77	28.77	28.73	28.73
	37	CH	PPPPP (<i>mmm</i>)	28.66	28.66	28.62	28.62
	36	CH	PPPPP (<i>rrm</i>)	28.54	-	-	-
	35	CH	PPPPP (<i>rrm</i>)	28.46	-	28.48	-
	34	2B ₂	PPBP	28.27	28.27	28.25	28.25
	33	2B ₂	BPBP	28.24	overlap	28.22	28.22
			BPBP				
	32	2B ₂	XPBPX	28.07-27.98	28.03-28.0	28.05-27.96	28.05-27.97
	31	$\beta\delta$	EPEE	27.49	27.49	27.46	27.46
	30	$\beta\delta$	PPEE	27.26	27.26	27.25	27.25



Table 1 Continued.

Region	Peaks No.	Carbon	Polymer sequence	¹³ C (ppm)			
				Terpolymer A	Terpolymer B	Terpolymer C	Terpolymer D
C	29	ββ	PPEPE	24.64	24.65	24.63	24.63
	28	ββ	XPEPX	24.58	24.58	24.56	24.56
	27	ββ	PPEPP(m)	24.51	24.51	24.49	24.49
	26	ββ	PBEBP	24.29	24.29	24.25	24.25
B	25	1B ₁	PPPPP (xxxx)	21.98	21.98	21.97	21.97
	24	1B ₁	PPPPP (mmmm)	21.81	21.81	21.80	21.80
	23	1B ₁	PPPPB	21.79	21.78	21.77	21.77
	22	1B ₁	BPPPB+PPPPP (xmmm)	21.75	21.75	21.74	21.73
	21	1B ₁	PPBPB	21.69	21.69	21.68	21.68
	20	1B ₁	BBPPP+PBPPB	21.66	21.66	21.65	21.65
	19	1B ₁	PPPPP (xmrx)	21.63	21.63	21.61	21.62
	18	1B ₁	PPPPP (xrxx)	21.58	21.58	21.56	21.56
	17	1B ₁	PBPBP	21.56-21.51	21.56-21.52	21.55-21.50	21.55-21.50
		1B ₁	PPPPP (xmrx)				
	16	1B ₂	XPBPX	21.46	21.46	21.46	21.46
	15	1B ₃	XPBPX	21.39	21.39	21.38	21.38
	14	1B ₁	PPPPP (xrmx)	21.02	21.02	21.00	21.00
	13	1B ₁	PPPEP	20.89	20.89	20.88	20.88
	12	1B ₁	XPPEX	20.86	20.86	20.85	20.85
	11	1B ₁	XPPEX	overlap	20.84	20.83	20.83
	10	1B ₁	XPPEX	20.76	20.77	20.75	20.75
9	1B ₁	XPPEX	20.71	20.71	20.69	20.69	
8	1B ₁	PPPPP (xrxx)	-	20.01	20.00	20.00	
7	1B ₁	PPPPP (xrxx)	19.87	-	19.86	-	
	*	unusual structure	18.49	-	-	-	
A		*	unusual structure	11.46	-	-	-
	6	1B ₂	EBE	11.20	11.21	11.21	11.21
	5	1B ₂	PPBPP	11.06	11.05	11.05	11.06
	4	1B ₂	XPBPX	11.04	11.04	11.04	11.04
	3	1B ₂	BBE+XPBPX	11.02	11.01	11.01	11.01
	2	1B ₂	PPBBP	10.98	10.99	10.99	10.99
1	1B ₂	XPBBX	10.96	10.96	10.96	10.96	

X are ethylene, propylene or butene monomer units

x are *meso(m)* or *racemic(r)*

*Unusual structures are unexpected structures that could be produced by the degradation process or unexpected reactions

3.4 gHSQC, gHMBC and gHSQC-TOCSY 2D NMR spectra of poly(ethylene-co-propylene-co-butene)

2D NMR phase-sensitive gHSQC spectrum (between $\delta_C = 10 - 50$ ppm and $\delta_H = 0.7 - 1.8$ ppm) of terpolymer A obtained at 400 MHz instrument shown in Figure 5. The gHSQC spectrum provides one bond correlation between ¹H and directly bonded ¹³C. The methine (CH)/methyl (CH₃) and methylene (CH₂) carbons can be easily distinguished in the phase-sensitive gHSQC spectrum. The red color cross-peaks are from the methine/methyl carbons and the blue color cross-peaks are from the methylene carbons. The expansion of the corresponding region from the 1D ¹H and ¹³C spectra are displayed on the left side and on the top of the 2D spectrum. The 2D gHSQC spectrum assignments initially were made based on literature [7-14]. The correlations from gHSQC, gHSQC-TOCSY and gHMBC spectra help to confirm most of the assignments, corrections and new assignments of the resonances.

Recently, multidimensional NMR has become a powerful method for studying the tacticity of polymers. The differences in the chemical shifts of the $\alpha\alpha$ methylene protons in *meso* and *racemic* structures are the key for investigating the stereo-sequence assignments. In a *meso* (*m*) structure, the two $\alpha\alpha$ methylene protons are not identical, thus two methylene protons resonances are observed whereas in a *racemic* (*r*) structure, the two $\alpha\alpha$ methylene protons are approximately identical and therefore only one methylene proton resonance is observed. In this work, the tacticity of poly(ethylene-co-propylene-co-butene) terpolymers were successfully assigned.

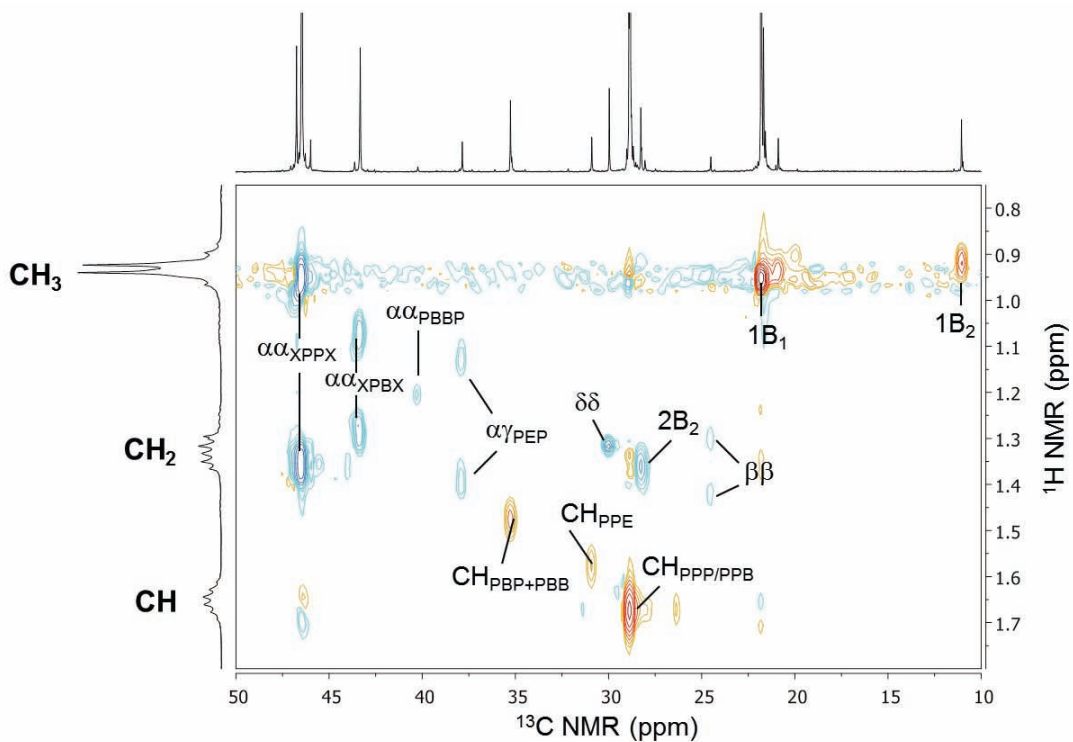


Figure 5 The gHSQC spectrum of terpolymer A.

Figure 6 shows the expansion from the gHSQC spectrum of terpolymer A obtained at 500 MHz between $\delta_C = 40 - 47$ ppm and $\delta_H = 0.8-1.6$ ppm. These cross-peaks are assigned to $\alpha\alpha$ methylene of PBBP (cross-peak a), XBPX (cross-peak b/b', c/c' and d/d'), and XPPX (cross-peak e/e', f/f' and g/g'), monomer sequence, respectively (X are B or P unit). The $\alpha\alpha$ methylene protons of PP and PB centered dyads are resulted in difference proton resonances (cross-peak b/b' to g/g'). It is indicated that terpolymer A contains mainly *meso* structure. However, the $\alpha\alpha$ methylene protons of BB centered dyads (cross-peak a) contribute to a single proton resonance of equivalent methylene protons and, thus this peak is assigned to the *racemic* structure of PBBP monomer sequence.

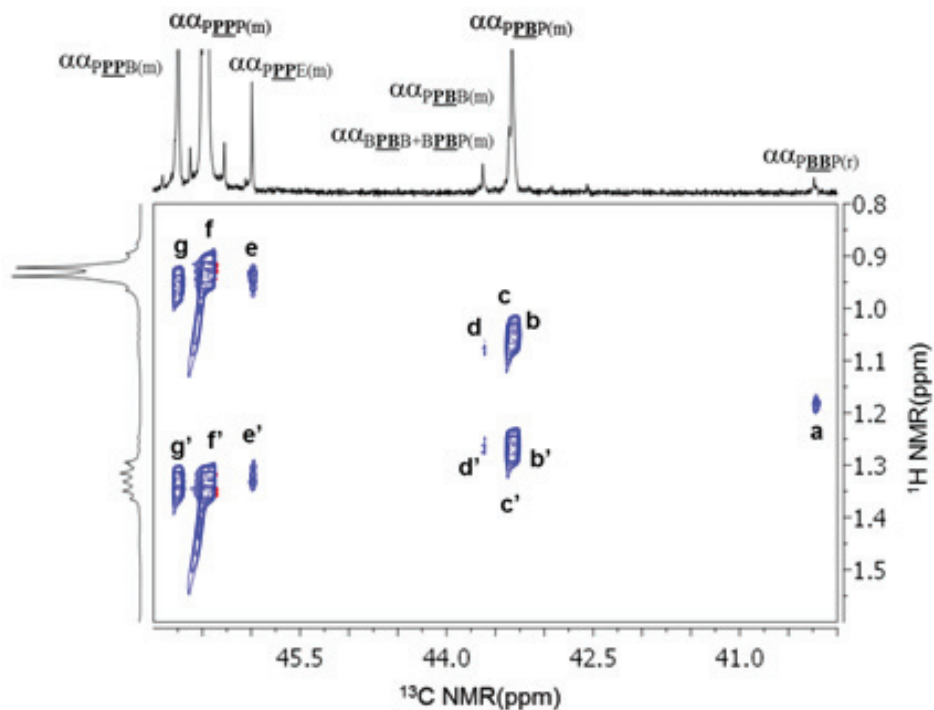
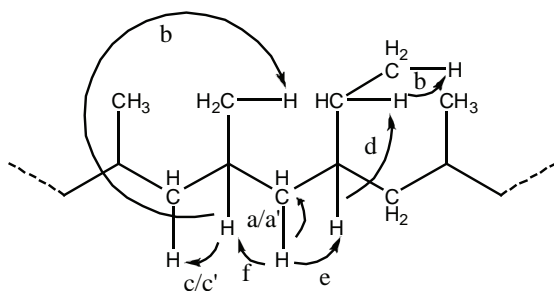


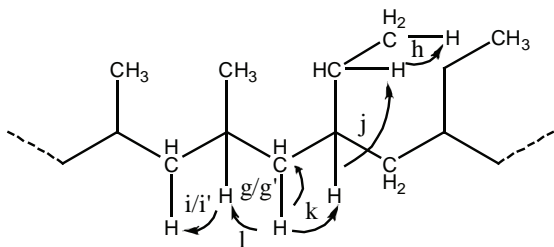
Figure 6 The expansion from the gHSQC spectrum of terpolymer A in the $\alpha\alpha$ methylene region obtained from 500 MHz instrument.

Figure 7 shows the expansion from the gHSQC-TOCSY spectrum of terpolymer A in the $\alpha\alpha$ methylene region of $XPBX$ monomer sequences obtained from 500 MHz instrument. The gHSQC-TOCSY spectrum shows one bond proton-carbon correlations (cross peaks in blue area) and the correlations onto neighboring protons within the same spin system. The chemical structures show the connectivity in this region is displayed on the top of the 2D NMR spectrum. Cross-peaks a/a' arise from the C-H correlation of $\alpha\alpha$ methylene from $PPBP$ monomer sequence. These protons show correlation to $1B_2$ (cross-peak b), $\alpha\alpha_{XPPX}$ (cross-peaks c/c'), $2B_2$ (cross-peak d), CH_{PPB} (cross-peak e) and CH_{PPB} (cross-peak f) protons, respectively. The correlation of these protons to neighboring $\alpha\alpha$ methylene protons from PB dyad could not be seen in this experiment due to the overlapping of HSQC and TOCSY cross-peaks. These evidences suggest that $PPBP$ monomer sequence has a *meso*-centered stereo-sequence.

Cross-peaks g/g' arises from the C-H correlation of $\alpha\alpha$ methylene from $PPBB$ monomer sequence. These protons show correlations to $1B_2$ (cross-peak h), $\alpha\alpha_{XPPX}$ (cross-peak i/i'), $2B_2$ (cross-peak j), CH_{PPB} (cross-peak e) and CH_{PPB} (cross-peak f) protons. It is indicating that $PPBB$ monomer sequence contains *meso*-centered stereo-sequence.



PPBP



PPBB

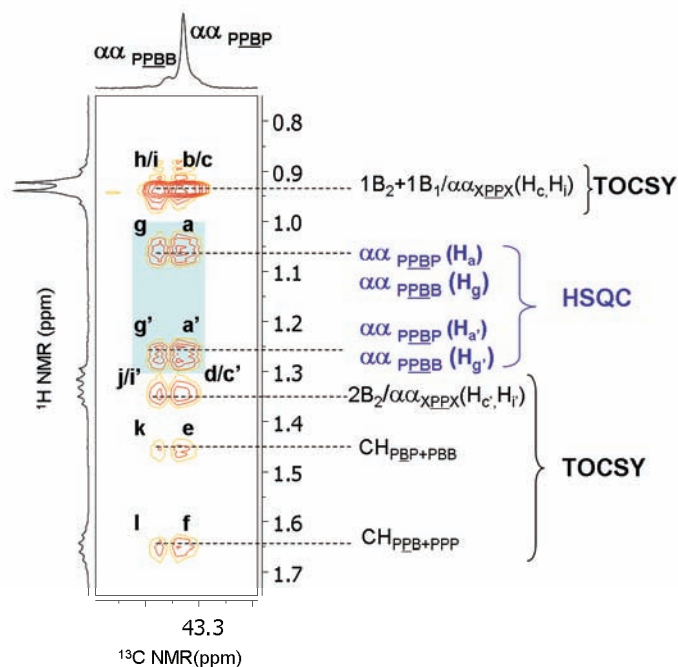


Figure 7 The expansion from the gHSQC-TOCSY spectrum of terpolymer A in the $\alpha\alpha$ methylene region of PPBP and PPBB monomer sequences.

The complete assignments of 2D NMR spectra of polymer A, B, C, and D were made by using the methodology similar to that described above.



4. Conclusion

In this work, it was demonstrated that the combination of 1D and 2D NMR experiments, including ^1H , ^{13}C , gHSQC, gHMBC and gHSQC-TOCSY, permitted the characterization of the complex microstructure of poly(propylene-co-ethylene-co-1-butene) polymers. These results confirm most of chemical shift assignments in the literatures. Newly resonances also found and assigned in this work. The differences in the chemical shift of the $\alpha\alpha$ methylene protons in *meso* and *racemic* structures were the key for investigating the stereo-sequence assignments. The completed ^{13}C NMR assignments permitted more accurate quantitative analysis of the microstructure in these polymers. The NMR data suggest that terpolymer A/C and terpolymer B/D could be produced with the similar processing condition.

5. References

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